

tyl esters of acrylic and methacrylic acid hydrogenate more rapidly than the corresponding methyl esters it seems unlikely that this effect could be due to a gradual decrease in solubility of the various acids. Moreover, decreasing solubility would not explain the abrupt change in the rate from the six to the eight carbon acids. There is a possibility that these variations may be due to steric factors which are dependent on the length of the carbon chain or possibly there may be some sort of micelle formation in the higher acids.

In order to further compare the Rh and Pd catalysts an attempt was made to hydrogenate various aliphatic nitro compounds. Both catalysts were ineffective for the reduction of nitromethane, nitroethane and 1-nitropropane. Rhodium but not palladium catalyzed the reduction of 2-nitropro-

pane at a very slow rate. It thus appears that for Pd to function a higher electron density must be present for the unsaturated compound to be adsorbed by the catalyst. This assumption was checked by hydrogenating a mixture of 2-nitropropane and *n*-butyl acrylate with both palladium and rhodium. The addition of the nitro paraffin caused no variation in the rate of hydrogenation with Pd. With rhodium, however, the rate of hydrogenation was decreased by about 30% indicating that the 2-nitropropane is not adsorbed by palladium.

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[CONTRIBUTION NO. 245 FROM THE DEPARTMENT OF ORGANIC CHEMISTRY AND ENZYMOLOGY, FORDHAM UNIVERSITY]

Investigations on the Mechanism of Catalytic Hydrogenations.¹ XVII. Reductions with Rhodium on Activated Carbon

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The reduction of various functional groups with a 5% rhodium on activated carbon catalyst has been investigated. This catalyst is useful for the reduction of the carbon-carbon double bond, activated nitro, carbonyl and nitrile groups, and quinones. It is also useful for the reduction of the various intermediates in the nitrobenzene to aniline system. A study of the rate of reduction of substituted nitrobenzenes to substituted anilines with this catalyst has shown that both the nature and position of the substituent alter the rate.

Introduction

Although noble metals have long been recognized as superior hydrogenation catalysts, little information is available regarding the catalytic properties of rhodium. It was reported,² however, that oriented rhodium films catalyze the hydrogenation of ethylene more rapidly than similar films of other metals. Previous work in this Laboratory³ has also demonstrated that polyvinyl alcohol-supported colloidal rhodium and palladium possess strikingly different properties when applied as hydrogenation catalysts. To further study the catalytic properties of rhodium we have investigated the hydrogenation of various organic compounds with the aid of an activated carbon catalyst containing 5% of the metal.

Experimental

The organic compounds employed in this investigation were obtained in the following ways. Nitrobenzene, the substituted nitrobenzenes, azobenzene, azoxybenzene, crotonic acid, the quinones, ethyl cyanoacetate, benzonitrile, aniline, benzophenone, styrene and benzaldehyde were commercially available preparations of the highest purity. The nitroparaffins were obtained through the courtesy of the Commercial Solvents Corporation, hexaldehyde and diisobutyl ketone from Carbide and Carbon Chemical Corporation, and the acrylic esters from Rohm and Haas Company. Nitrosobenzene, hydrazobenzene and phenylhydroxyl-

amine were synthesized in the laboratory. The various unsaturated acids: namely, α,β -hexenoic acid⁴; α,β -unsaturated eight-, ten- and twelve-carbon acids⁵; vinyl acetic acid⁶; β,γ -hexenoic acid⁷; γ,δ -pentenoic acid⁸ and γ,δ -hexenoic acid⁹ were also synthesized. The physical properties of all the compounds employed agreed with those reported in the literature. Five per cent. rhodium on activated carbon, lot #345 Baker & Company, was used for all experiments except for the reduction of quinones, the carbonyl group and the study of the concentration of the catalyst on the rate of hydrogenation of nitrobenzene. In these experiments lot #572 of the same catalyst was employed.

The hydrogenations reported here were carried out in a glass hydrogenation vessel at atmospheric pressure and room temperature.

The flask was shaken at a speed of 258 strokes/min. and the reaction followed volumetrically using water as the retaining liquid.

In each experiment 0.2000 g. of fresh catalyst was used. An initial study showed that if the catalyst was weighed to the fourth decimal and a standardized procedure adhered to, the rate studies were reproducible to within 5 to 10%. This method seemed preferable to re-using the same catalyst specimen since the former procedure eliminated the possibility of accidental contamination. Both procedures were used however in the study of the fatty acids.

In actual practice 0.2000 g. of catalyst was placed in the hydrogenation vessel and then 25 ml. of absolute alcohol was added. The vessel was then flushed with hydrogen, closed and shaken for 15 minutes. During this time ap-

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(6) L. Falaise and R. Frongnier, *Bull. soc. chim. Belg.*, **42**, 427 (1933).

(7) R. P. Linstead, *et al.*, *J. Chem. Soc.*, 740 (1931); 557 (1933).

(8) E. Schjanberg, *Ber.*, **70B**, 2385 (1937).

(9) E. N. Eccott and R. P. Linstead, *J. Chem. Soc.*, 2156 (1929).

(1) Presented before the Symposium on Catalysts held at the Diamond Jubilee Meeting of the American Chemical Society, September, 1951.

(2) O. Beeck, "Advances in Catalysis," Vol. 2, Academic Press, Inc., New York, N. Y., p. 151, 1950.

(3) L. Hernandez and F. F. Nord, *Experientia*, **3**, 489 (1947); *J. Colloid Sci.*, **3**, 363 (1949).

proximately 100 ml. of hydrogen was absorbed.¹⁰ Shaking was then stopped and the compound to be hydrogenated introduced together with 25 cc. of 95% alcohol. In some cases it was necessary to employ larger quantities of alcohol to effect solution. The same ratio of absolute to 95% alcohol was still maintained. Two-gram samples of the fatty acids, esters and intermediates in the reduction of nitrobenzene were employed, while 1-g. samples of all the other compounds were used.

Isolation of the Reaction Products.—When the products of hydrogenation were solids the solution was filtered with the aid of suction to remove the catalyst and the filtrate evaporated *in vacuo* to dryness. The residue was then dried in a desiccator. The melting point was taken, and if it did not correspond to an authentic sample, the residue was recrystallized from the appropriate solvent. When hydrazobenzene was the expected product, water was placed in the filter flask so that most of the hydrazobenzene would be immediately precipitated. This procedure minimized its oxidation to azobenzene.

Most of the amines were isolated as their acetyl derivatives. These derivatives were obtained by filtering the hydrogenation mixture, cooling the filtrate in an ice-bath and then adding cracked ice directly to the filtrate. Fifteen ml. of acetic anhydride was then added in one portion. The solution was kept in the ice-bath for 0.5 hour and then allowed to warm to room temperature. It was then evaporated *in vacuo* to dryness. Alcohol was then added and the solution again evaporated to dryness. The residue was recrystallized from aqueous ethanol. The yields of recrystallized material obtained by this method were about 70%. The remaining compounds were isolated by distillation.

Identifiable compounds could not be obtained from *p*-nitrobenzotrile and the nitrobenzaldehydes. Thus *p*-nitrobenzotrile gave an orange product almost insoluble in alcohol and ether but somewhat soluble in acetone which softened at about 180° but did not melt completely at 220°. The *p*-nitrobenzaldehyde yielded an orange-red solid that did not melt below 300°. *m*-Nitrobenzaldehyde absorbed only about 100 ml. of hydrogen during the first hour and then absorption ceases. The resulting product could be separated into an ether soluble portion which melted at 43° and an ether-insoluble residue which melted from 138 to 165°. The *o*-nitrobenzaldehyde yielded an oil which formed a solid mercury addition compound, which, however, had no definite melting point (145–180°).

Discussion and Results

Hydrogenation of the Carbon-Carbon Double Bond.—In Table I are summarized the results of this investigation.

TABLE I

REDUCTION OF THE CARBON-CARBON DOUBLE BOND

Compound	Hydrogen uptake in ml./min.
α,β -4 carbon unsaturated acid	115
α,β -6 carbon unsaturated acid	105
α,β -8 carbon unsaturated acid	120
α,β -10 carbon unsaturated acid	120
α,β -12 carbon unsaturated acid	105
β,γ -4 carbon unsaturated acid	90
β,γ -6 carbon unsaturated acid	90
γ,δ -5 carbon unsaturated acid	110
γ,δ -6 carbon unsaturated acid	110
Ethyl acrylate	105
Ethyl methacrylate	103
<i>i</i> -Butyl acrylate	100
Styrene	45

It can be seen from the recorded data that the rate of hydrogenation of the various acids and esters lies within much narrower limits than when the colloidal Rh catalyst is used. In the experiments with β,γ -hexenoic acid, however, the rate

(10) Since the amount of hydrogen absorbed in 15 minutes is virtually independent of the amount of catalyst used, *i.e.*, 0.1 → 1 gram, it appears that this absorption is due to an incomplete removal of air from the hydrogenation vessel. Thus the oxygen in the air is reduced to water by this preliminary treatment.

fell off during the hydrogenation. This was further studied by hydrogenating β,γ -hexanoic acid to completion (rate 90 ml./min.) and then adding a second portion of the acid to the hydrogenation mixture. When the hydrogenation of the second portion was complete a third portion was added and hydrogenated. The rate of hydrogenation of the second portion was nearly constant and amounted to 70 ml./min. The rate of the third portion, again rather constant, was 50 ml./min. The solution was then filtered and the catalyst repeatedly washed with absolute alcohol, and then air dried. It was then re-used for the hydrogenation of another sample of β,γ -hexenoic acid. The rate of this hydrogenation was similar to the rate of the first hydrogenation mentioned above. Previous work in this Laboratory has shown that β,γ -unsaturated acids are hydrogenated more slowly than the other unsaturated straight-chained isomeric acids using polyvinyl alcohol-supported rhodium catalyst, in 70% aqueous ethanol. The present experiments indicate that this is also the case with rhodium on carbon in 98% alcohol. It is to be noted however that the solvent employed in these studies would minimize the ionization and hence any variations in rate that may be due to ionization.

Reduction of the Nitro Group.—Nitrobenzene is smoothly reduced to aniline with the aid of the rhodium catalyst. The rate of reduction of the nitro group however is considerably slower than that at which the carbon-carbon double bond is reduced. Thus in 30 minutes 128 ml. of hydrogen was absorbed. The rate however is sensitive to changes in the pH of the solution. Thus when 1 ml. of glacial acetic acid is added to the hydrogenation mixture absorption increases to 183 ml. for 30 minutes and when 1 ml. of 10% potassium hydroxide is added 425 ml. of hydrogen is taken up in the same time interval. It was also noted that the rate increased during an individual hydrogenation presumably on account of the basicity of the aniline formed. This was confirmed when 0.5 ml. of aniline was added to the hydrogenation mixture. The absorption in 30 minutes was then 208 ml. These experiments were carried out with a different batch of catalyst and equated to the above results. In Table II are recorded the values for the rate of hydrogen absorption of nitrobenzene observed with varying catalyst concentrations.

TABLE II

VARIATION IN THE RATE OF REDUCTION OF NITROBENZENE WITH THE CONCENTRATION OF THE CATALYST

Concentration of catalyst, g.	Hydrogen absorption in 0.5 hour
0.1000	77
.2000	153
.3000	250
.5000	508

1-Nitrobutane and 2-nitropropane absorbed 25 and 10 ml. of H₂, respectively, in 30 minutes. However, no reduction products were isolated. This indicates that the electron-releasing power of the phenyl group considerably enhances the rate at which the nitro group is reduced.

In Table III are recorded the rates at which substituted nitrobenzene derivatives are hydrogenated.

TABLE III

REDUCTION OF SUBSTITUTED NITROBENZENES

Substituent and position	H ₂ uptake in ml. per 30 min.
<i>p</i> -CH ₃ (1 ml. HOAc)	170
<i>p</i> -CH ₃	117
<i>o</i> -NH ₂	108
<i>o</i> -NH ₂ (1 ml. HOAc)	72
<i>m</i> -NH ₂	229
<i>p</i> -NH ₂	100
<i>p</i> -CHO	103
<i>m</i> -CHO	47
<i>o</i> -CHO	200
<i>p</i> -Cl	67
<i>p</i> -COOH	328
<i>p</i> -OH	283
<i>p</i> -OCH ₃	91
<i>p</i> -CN	79

The reduction products of the compounds listed in Table III were isolated and identified either directly as the amine or through their acetyl derivatives except for the substituted nitriles and aldehydes, which yielded mixtures. From these experiments it appears that the rhodium catalyst is incapable of selectively hydrogenating the nitro group in the presence of either the aldehyde or nitrile functions.

In the case of *p*-chloronitrobenzene the reaction product was again a mixture. This is the result of the competing hydrogenation and dehalogenation reactions. Upon further studying this reaction by hydrogenation 10 g., of *p*-chloronitrobenzene with 0.5 g. of rhodium on carbon, a yield of 95% *p*-chloronitrobenzene was obtained. When 1 g. of *p*-chloronitrobenzene was hydrogenated with 1 g. of the same catalyst 0.6 g. of an ether insoluble product was obtained, which melted at 198–200° and gave an immediate precipitate with an aqueous solution of AgNO₃ thus indicating that a dehalogenation had occurred since the product was obviously a hydrochloride.

A consideration of the variation in rate with the nature and position of the substituent shows that both these factors influence the rate. It appears that the electron-releasing groups in the ortho and para position tend to decrease the rate, while either acidic or basic groups tend to increase the rate. These two effects appear to be competing since *p*-nitroaniline hydrogenates slowly, while *p*-nitrophenol hydrogenates rapidly. On the other hand *p*-nitroanisole hydrogenates slowly, while *m*-nitroaniline hydrogenates rapidly. A discussion of the rate of hydrogenation of the nitrobenzaldehydes and nitrobenzotrile is impeded by the fact that the products of partial hydrogenation are insoluble. The same is the case with *p*-chloronitrobenzene since here, as mentioned, we have two competing reactions (hydrogenation and dehalogenation).

Hydrogenation of Intermediates in the Reduction of Nitrobenzene.—Since it is generally agreed^{11–13} that nitrobenzene is neither catalytically nor electrochemically reduced directly to aniline but rather passes through definite intermediate compounds, it was thought that a study of the rate of reduction of these compounds with rhodium might further elucidate the mechanism of the reduction of nitrobenzene itself. The results of this study are recorded in Fig. 1.

Since these reductions were not carried out in an alkaline medium the formation of condensation products was not to be expected. However, when nitrosobenzene was partially reduced azoxybenzene could be isolated from the reduction mixture. This product was identified by its melting point, mixed melting point and conversion into azobenzene by heating with PCl₅. Since it is known that phenylhydroxylamine and nitrosobenzene condense to form azoxybenzene this indicates that phenylhydroxylamine is an intermediate in the reduction of nitrosobenzene.

Phenylhydroxylamine appears to be directly reduced to aniline. When azoxybenzene is reduced both aniline and hydrazobenzene can be isolated from the reduction mixture, the same products can also be isolated when azobenzene is reduced. Hydrazobenzene yields aniline.

Hydrogenation of the Carbonyl Group.—The results of this study are recorded in Table IV.

Compound hydrogenated	Hydrogen uptake in ml./30 min.
Hexaldehyde	0
Phenylacetaldehyde	0
Diisobutyl ketone	0
Benzaldehyde	176
plus 1 ml. 10% KOH	25
plus 1 ml. HOAc	210
Benzophenone	13

From the total hydrogen absorption and qualitative indications toluene was considered to be the product of hydrogenation of benzaldehyde, although it was not isolated. Benzophenone yielded diphenylmethane. It appears from

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 (12) G. Vavon and Crajinovic, *Compt. rend.*, **187**, 420 (1928).
 (13) F. Haber and G. Schmidt, *Z. physik. Chem.*, **32**, 193, 271 (1900).

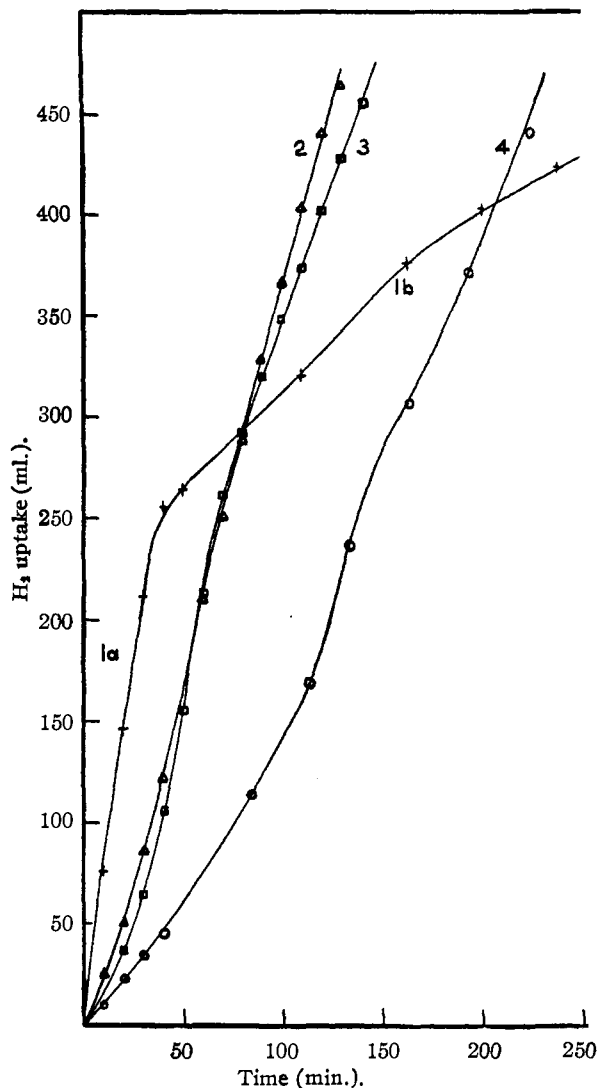


Fig. 1.—Hydrogenation of intermediates in the reduction of nitrobenzene; 1a, azobenzene to hydrazobenzene; 1b, hydrazobenzene to aniline; 2, nitrobenzene and phenylhydroxylamine; 3, nitrosobenzene; 4, azoxybenzene.

the above table that the carbonyl function must be activated in order for hydrogenation to occur. The Rh on activated carbon catalyst has proven to be excellent for the reduction of quinones. In Table V are summarized the results of this study.

Compound hydrogenated	Hydrogen absorption
Quinone	40 ml./min.
plus 1 ml. concd. HCl	110 ml./hr.
plus 1 ml. HOAc	26 ml./min.
<i>p</i> -Toluquinone	145 ml./min.
Naphthoquinone	100 ml./min.

Hydrogenation of the Nitrile Group.—Under the conditions employed in this study benzonitrile is reduced to dibenzylamine. The initial rate for this reduction is 70 ml. in the first half-hour but falls off as the hydrogenation proceeds. Ethyl cyanoacetate is reduced¹⁴ at approximately the same rate and also shows the same decrease in rate. This decrease may be caused by the ammonia that is formed in the condensation to the secondary amine.

(14) K. E. Kavanagh, *THIS JOURNAL*, **66**, 2126 (1944).

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The Hydrolysis of Optically Active Secondary Butyl Hydrogen Sulfate¹

BY ROBERT L. BURWELL, JR.

At 100° (+)sodium *s*-butyl sulfate hydrolyzes slowly in basic solutions to give an alcohol of inverted configuration. Since the rate is nearly independent of the hydroxide ion concentration, a rearward displacement of sulfate ion by a water molecule seems to be involved. In acidic solution, a much more rapid hydrolysis leads to a partially racemized alcohol of retained configuration. The degree of racemization of the 2-butanol is influenced by the acid employed as catalyst and by other conditions. The fraction of the alkyl sulfate diverted to butylene varies similarly.

Hydrolysis of dextrorotatory salts of *s*-butyl hydrogen sulfate yields (+)2-butanol² in acid solution, but (–)2-butanol in basic solution.³ Such an apparent change in mechanism is rare, particularly for singly substituted alkyl derivatives, and therefore the stereochemistry of the hydrolysis as a function of the acidity of the solution has been

studied in detail. Interpretation of results has been facilitated by the recent demonstration⁴ that (+)2-butanol is most probably configurationally related to (+)sodium *s*-butyl sulfate.

Experimental

(+)Sodium *s*-butyl sulfate was prepared from partially resolved (+)2-butanol.⁴ Recovered alcohol was equilibrated with a saturated solution of potassium carbonate dihydrate⁵ before polarimetry. Configurations were correlated by equating optically pure (+)2-butanol, $[\alpha]_D^{25} +10.97^\circ$, to optically pure (+)sodium *s*-butyl sulfate, $[\alpha]_D^{25} +10.7^\circ$ (aqueous solution, *c* 26).⁴

Hydrolysis Apparatus.—Hydrolyses were run in the apparatus shown in Fig. 1. Reactants were added through B. Flask A was either heated directly by a micro-burner or immersed in a steam-bath and the riser tube C-D heated by a winding of Nichrome ribbon, in each case to such a degree that a mixture approximating the alcohol-water azeotrope could just distill out. The volume of the distillate

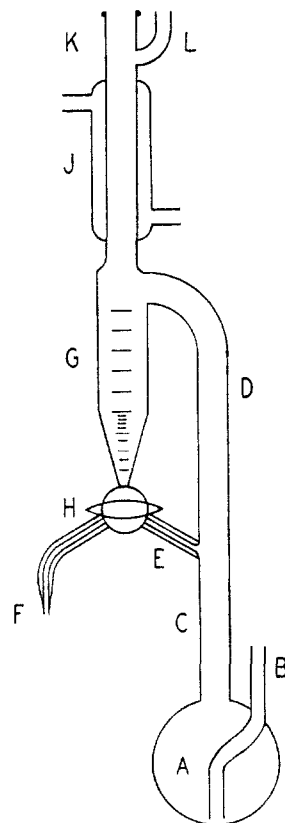


Fig. 1.—Hydrolysis apparatus.

(commonly two phase with the alcohol rich phase in greater proportion) was measured in the receiver G prepared from a graduated 12-cc. centrifuge tube. Outlet L was connected to a gas buret.

(1) Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society, Atlantic City, N. J., September 21, 1949.

(2) R. L. Burwell, Jr., *THIS JOURNAL*, **67**, 220 (1945).

(3) R. L. Burwell, Jr., and H. Holmquist, *ibid.*, **70**, 878 (1948).

(4) R. L. Burwell, Jr., *ibid.*, **71**, 1769 (1949).

(5) R. L. Burwell, Jr., *ibid.*, **64**, 1025 (1942).

For slow reactions ($t_{1/2} > 1$ day), heating on a steam-bath was satisfactory but for more rapid reactions the rate of alcohol collection fell behind. Where the solution in A was kept refluxing, however, it was possible to keep the alcohol and butylene contents of the reaction flask at very low values even for reactions whose time of half reaction was as little as five minutes. Rates of reaction, crude but nevertheless useful, could, thus, be obtained in addition to the primary stereochemical data.

Experimental Results.—Results of hydrolysis runs are presented in Table I. The amount of sodium *s*-butyl sulfate employed varied between 0.023 and 0.037 mole. All of the runs in acid solutions were at the former figure. Precision in alcohol yield is about 4 percentage points; in butylene yield, about 2; and in optical purity, 0.5% or better.

The ethanesulfonic acid which was employed was obtained from the Indoil Chemical Company. In computations it was assumed pure but it was reported to contain 1% sulfuric acid.

Run 20.—A solution of 0.156 mole of sodium hydrogen sulfate, 0.078 mole of sodium sulfate, 0.0227 mole of (+)sodium *s*-butyl sulfate and 4.18 moles of water was refluxed 37 minutes and rapidly cooled. 6.3% alcohol and 4.4% butylene were evolved. The reaction mixture was neutralized with sodium hydroxide and extracted with methanol to give 82% of the original alkyl sulfate, optical purity +94.9%. The optical purity of the 2-butanol was –39% as found by weight dilution with inactive material to give enough material to examine. Recovered alkyl sulfate, made up into a solution of the same mole fraction composition as before, was refluxed 234 minutes to give alcohol, 34%, optical purity –31.6%; butylene, 14%; recovered alkyl sulfate, 34%; optical purity +66%. Upon ignition of the recovered alkyl sulfate followed by re-ignition with a drop of sulfuric acid, a weight loss of 56.9% was observed. The theoretical is 59.6%. If the only impurity was sodium chloride, it would, thus, amount to 3.4%. The optical purity of the recovered sodium *s*-butyl sulfate would then be +68%.

Run 21.—A sulfuric acid solution identical to run 9 was refluxed for 12 minutes and processed similarly. Alcohol amounted to 37%, optical purity +15.3%; recovered salt amounted to 26.5%; optical purity +77.3%. Loss on ignition was 57.2%. Chloride (inadvertently introduced during neutralization with sodium hydroxide which contained chloride) was found in the recovered salt. If all impurity was sodium chloride, it would amount to 3.1% and corrected optical purity of recovered alkyl sulfate would be 80%.

Table II presents initial rates of dehydration of 2-butanol by sulfuric acid and by ethanesulfonic acid as measured by the rate of gas evolution with solutions of the indicated composition held at reflux. The initial boiling point is given but this presumably rises as the alcohol concentration declines. Several similar mixtures were prepared from (+)2-butanol. When about 21% of the stoichiometric quantity of butylene had been evolved, a sample of alcohol was rapidly distilled from the mixture by slightly increasing the heating. Its optical purity was then determined as given in the last column of Table II.

Discussion

The hydrolysis of optically active sodium *s*-butyl